LCA Methodology

Nutrient Loads to Surface Water from Row Crop Production

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Abstract

Goals, Scope and Background. Eutrophication and hypoxia, which are already serious environmental issues in the Midwestern region of the United States and the Gulf of Mexico, could worsen with an increase emphasis on the use of corn and soybeans for biofuels. Eutrophication impacts from agriculture are difficult to integrate into an LCA due to annual variability in the nutrient loads as a factor of climatic conditions. This variability has not been included in many relevant energy or row crop LCAs. The objective of this research was to develop a relatively simple method to accurately quantify nutrient loadings from row crop production to surface water that reflects annual variations due to weather. A set of watersheds that comprise most of eastern Iowa was studied. Ample data describing corn-soybean agriculture in this region and nutrient loadings to the Mississippi River enabled the development, calibration and validation of the model for this particular region.

Methods. A framework for estimating lifecycle inventory data for variable nutrient loading from corn-soybean agriculture was developed. The approach uses 21 years of county-average data for agricultural and annual rainfall for 33 counties that approximate three major watersheds in eastern Iowa. A linear equation describes the relationship between the fraction of the applied nutrients that leach into the surface water and the annual rainfall. Model parameters were calibrated by minimizing the error in the difference between actual and modeled cumulative discharge to the Mississippi River over the period 1988–1998. Data from 1978–1987 were used to validate the method. Two separate approaches were then used to allocate the nutrient flows between the corn and soybeans.

Results and Discussion. The total nitrogen (TN) and total phosphorus (TP) leaching models provide good representation of the variability in measured nutrient loads discharged from eastern Iowa watersheds to the Mississippi River. The calibrated model estimates are within 1.1% of the actual 11-year cumulative TN load and 0.3% of the TP load. In contrast, a standard method used in other lifecycle assessments for estimating nutrient leaching based on a constant fraction of the nutrients leached provides a reasonable average, but does not capture the annual variability. Estimates of the TN load that can be allocated to corn range from 60 and 99% between two allocation methods considered. This difference stems from a poorly understood symbiosis of nitrogen flows within the corn-soybean rotation that is difficult to integrate into an LCA.

Conclusions. Lifecycle inventories can include improved estimates non-point source nutrient flows to surface waters by incorporating climatic variability. Nutrient discharges to surface water are estimated with emission factors as a linear function of the annual rainfall rate. Water quality data is required to calibrate this model for a given region. In comparison with a standard approach that uses an average emission factor, the model presented here is superior in terms of capturing the variability that is correlated to an increase in the size of the hypoxic zone in the Gulf of Mexico.

Recommendations and Perspectives. Lifecycle inventories quantifying nutrient discharges from corn-soybean production should include the variability in these flows that occur due to climatic conditions. Failure to do so will reduce the LCA's capability of quantifying the very significant eutrophication and hypoxia impacts associated with wet years.

Keywords: Biofuels; corn; eutrophication; hypoxia; non-point source pollution; nutrient leaching; soybean; water quality

Introduction

Fertilizers used to increase the yield of row crops used for food or biofuels can migrate through the environment and potentially cause adverse environmental impacts. Nitrogen fertilizers have a complex biogeochemical cycle. Through their transformations and partitioning among environmental compartments, they contribute to eutrophication of surface waters at local and regional scales, groundwater degradation, acid rain, and climate change. Phosphate fertilizers have a simpler fate in the environment, although leaching of soluble and bound phosphorus is an important contributor to eutrophication.

Row crop production in the Midwestern region of the USA contributes the highest fluxes of nitrogen and phosphorus to the Mississippi River basin [1] and is considered one of the primary contributors to the growing hypoxic zone in the Gulf of Mexico. Through a combination of excessive nutrient loads and hydrodynamic conditions, a region along the coast of Louisiana that is approximately the size of the State of Massachusetts is considered ecologically dead most summers [2]. Variability in the nutrient loads to the Gulf of Mexico is highly dependent on the annual mean river discharge [1], which in turn is a direct consequence of variability in the annual rainfall in the Midwest each year. Indeed, numerous field studies [3–7] have quantified the substantial variation in nutrient leaching during years of light versus heavy rainfall. The higher nutrient loads observed during wet years are also somewhat correlated to the size of the hypoxic zone in the Gulf of Mexico [2,8].

Highly sophisticated hydrologic and agricultural models can be used to estimate the fate of nitrogen and phosphate nutrients in row crop systems and their subsequent fate downstream in surface water bodies. Mechanistic models for nu-

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trient flows attempt to explicitly model the non-linear interrelationships between these flows and nutrient use, crop productivity, weather patterns, and geographic conditions. Application of this type of model requires a vast set of site-specific parameters to quantify all of these interrelationships. SWAT (soil water assessment tool), for example, is one of the most comprehensive watershed models currently available [9], especially when linked to a model such as EPIC (erosion productivity impact calculator) that estimates field-scale crop growth, N and P cycling, runoff and erosion [10]. SWAT has been applied to watersheds in central Iowa to predict the effectiveness of changes in agricultural practices on the reduction in erosion and nitrate loads to surface waters [11]. Models such as this require short time steps to delineate erosion and nutrient flows caused by individual rainfall events because even short term rain events can cause much longer-term discharges of nutrients to surface water bodies [12–13]. This degree of detail is necessary if the environmental impacts of concern also occur at the same time scale. Eutrophication and hypoxia, however, have been correlated to seasonal or annual cumulative nutrient discharges [14].

Empirical emission factor approaches provide an alternative means of estimating non-point source nutrient flows as a fraction of the fertilizer applied or other measure of anthropogenic inputs [15–18]. For example, the International Panel on Climate Control (IPCC) [19], which focuses on air emissions, recognized the need to quantify leaching to surface waters due to the subsequent denitrification and release of N_2O. The IPCC suggests that nitrogen leached to surface waters could be estimated as 30% of the applied fertilizer that remains after volatilization, although they recognize values could range from 10–80%. The greenhouse gas and air emission model (GREET) [15], used leaching rates measured at several different field test plots [e.g., 20–21] to estimated that 24% of the fertilizer nitrogen (FN) leaches to surface water. Neither of these widely used models incorporates variability in leaching rates as a function of precipitation or other climatic variation. Emission factors are easy to apply, and could be appropriate for simple systems such as phosphate discharges to surface water. However, they are less likely to capture complex interactions among various transformations and partitioning of nitrogen among environmental compartments, especially as a function of the variety of agricultural practices and geologic, hydrologic and weather conditions among different farming regions.

Integrating non-point source nutrient loads associated with agricultural activities into lifecycle inventory and impact assessments requires a balance between accuracy and reasonable simplicity. Mechanistic models such as those described above have not been used in agricultural life cycle assessments to date. This is most likely due to the extensive parameterization required (soil types, weather, agricultural practices etc.). On the other hand, emission factor approaches can fail to estimate the range of impacts associated with climatic and regional variability. Miller et al. [17] recently employed Monte Carlo techniques to provide statistical distributions of non-point source nitrogen inventory flows. This technique includes variability and uncertainty in each individual emission factor, but does not integrate the more direct functional relationships among the various nitrogen transformation and transport processes. The work presented in this paper provides another relatively simple empirical approach to integrating variability of nutrient discharges to surface water and the resulting eutrophication impacts.

1 Goals and Scope

With an increase interest in the use of corn and soybeans for fuel production, it is important to understand the relative environmental benefits and deleterious impacts associated with this growing market. A team of researchers lead by the U.S. DOE's National Renewable Energy Laboratory (NREL) completed life cycle assessments (LCA) for biodiesel [22] and ethanol from corn stover [23]. The stover report focused on the green house gas emission benefits associated with biofuels as balanced by potential detriments to soil health. Eutrophication was identified as an important issue by stakeholders, but limited resources prevented this environmental impact category from being addressed.

The overall goal of this research was to provide a tool to enable improved estimates of non-point source nutrient flows from row crop production that could be integrated into biodiesel or ethanol biofuel lifecycle assessment studies. The objectives of the research presented in this paper were to develop, calibrate and validate a simple emission factor-based means to accurately quantify nutrient loadings to surface water that reflects annual variations due to weather. This methodology was then used to quantify surface water quality impacts associated with nutrient fertilizers used for energy crop production. A set of watersheds that comprise most of eastern Iowa was chosen as the geographic region. Ample data describing corn-soybean agricultural practices in this region and nutrient loadings to the Mississippi River enabled the development and calibration of the model for this particular region.

Applying an agricultural LCA to a specific geographic location provides increased accuracy by using site-specific data. A balance must be made, however between a site that is so small that it is not representative of the broader system versus a region that is so large that input data and nutrient flows vary substantially over the region and are difficult to characterize. The eastern Iowa region selected for this study (**Fig. 1**) encompasses approximately 50 thousand km². It was chosen based on its high productivity of corn and soybeans, the availability of agricultural practice, yield, and erosion data, and its align-

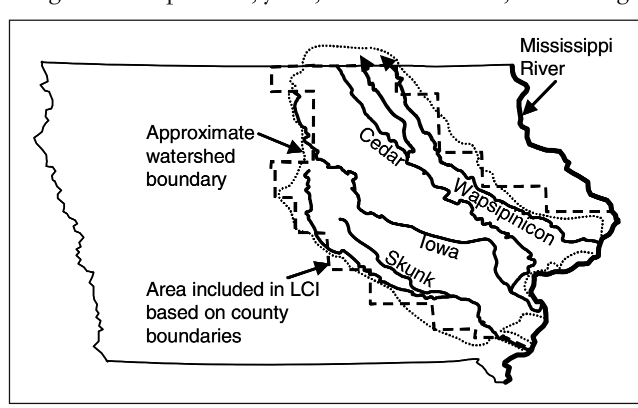

Fig. 1: Geographic scope of study area within the State of Iowa includes discharge of three major watersheds (Skunk, Iowa and Wapsipinicon) to the Mississippi River

ment with three major watersheds for which several years of water quality data exist. These data were essential for the development and calibration of nutrient leaching models.

County boundaries were used to define the geographic system boundary to approximate the overall area encompassing the Wapsipinicon, Skunk, Iowa and Cedar River watersheds. There is over one order-of-magnitude variation in stream flow among the 21 individual years considered (1978–1998), with the lowest flows in 1989 and the highest in 1993, corresponding to annual rainfall extremes. Data from 1988–1998 were used to develop and calibrate the leaching model, with data from 1978–1987 used to validate the overall process.

The geology, hydrology and land use practices in this region are described extensively by Becher et al. [24–25]. Overall, approximately 64% of the region is used for row crop production. This is mostly dedicated to corn-soybean rotations, although some farms, especially in the northeast and east central regions, practice corn-corn-soybean rotations [26].

Data describing agricultural practices and yields were readily available through the USDA National Agricultural Statistics Service (USDA NASS) electronic reports and databases. The inclusion of several years in this study allowed variability of crop yields and nutrient flows as a function of rainfall to be incorporated. The use of average data would have lost the important environmental impacts associated with extreme climatic conditions.

2 Methods

2.1 Quantification of actual nutrient loads to the Mississippi River

The eastern Iowa watershed system was selected as a geographic boundary due to the extensive data for total nitrogen (TN) and total phosphorus (TP) loads to the Mississippi River. The availability of these data provides an excellent means of calibrating and validating the nutrient flow model against real data. Leaching from fields and in-stream denitrification processes were both considered in this calibration process.

Data sets quantifying the TN and TP load were available from the USGS National Ambient Water Quality Assessment (NAWQA) [25] and the NOAA/USGS Hypoxia in the Gulf of Mexico study [27]. Neither of these data sets provides both TN and NO_3-N loads for all three watersheds of interest over the entire time period, so some of the loads were estimated based on statistical correlations. TN and TP loads are presented in **Table 1**. Values for the Cedar River – which is included within the overall Iowa River watershed – are included because they provided the best correlation for the fraction of TN load associated with the Wapsipinicon River. For the three years that a complete data set for all four watersheds was available [25], it was determined that the Wapsipinicon TN loads were approximately one-third

Table 1: Actual nutrient loads to the Mississippi River from E. Iowa watersheds

Year	Total Nitrogen (t/y)				Total Phosphorus (t/y)			
	Wapsipinicon	Iowa	Skunk	Cedar	Wapsipinicon	Iowa	Skunk	Cedar
Data used to validate model								
1978	6,990	58,332	26,469	19,970	319	2,661	1,751	700
1979	18,031	92,205	29,819	51,516	490	4,252	1,910	1,679
1980	11,185	45,342	11,098	31,957	226	1,981	638	992
1981	7,969	42,255	11,884	22,767	201	1,836	668	718
1982	17,255	115,248	41,275	49,300	523	4,509	2,381	1,478
1983	24,964	120,828	38,033	71,325	542	4,641	1801	2,241
1984	17,737	95,607	35,955	50,678	459	3,792	1,925	1,623
1985	6,290	44,659	19,346	17,970	191	1,702	827	522
1986	15,672	103,254	33,968	44,778	443	3,811	1,961	1,324
1987	3,865	36,485	1,6045	11,044	154	1,464	638	360
Data used to calibrate the model								
1988	2,200	20,179	5,087	6,290	81	913	146	236
1989	1,227	7,616	2,189	3,508	52	557	118	155
1990	9,514	69,219	22,483	27,196	354	3,108	1711	844
1991	19,618	96,879	22,729	56,079	416	3,777	1112	1,778
1992	13,841	88,422	23,860	39,564	326	2,893	1,295	1,027
1993	35,784	199,911	51,287	102,290	1,158	10,341	4,673	3,520
1994	9,336	46,969	8,026	26,688	172	1,711	365	683
1995	8,284	54,321	15,877	23,680	248	2,177	1,140	653
1996	9,990	57,600	30,000	31,900	540	2,360	3,960	1,560
1997	21,700	75,100	23,500	52,200	440	3,120	990	1,860
1998	31,100	154,000	49,400	97,000	476	3,930	4,140	2,470

1996–1998 data from Becher et al. [24]
1978–1995 data for Skunk, Iowa and Cedar Rivers from NOAA/USGS Hypoxia study
1978–1995, Wapsipinicon R. – Estimated based on 0.35 * $TN_{(Cedar)}$, 0.062 * $TP_{(Cedar+Skunk+Iowa)}$

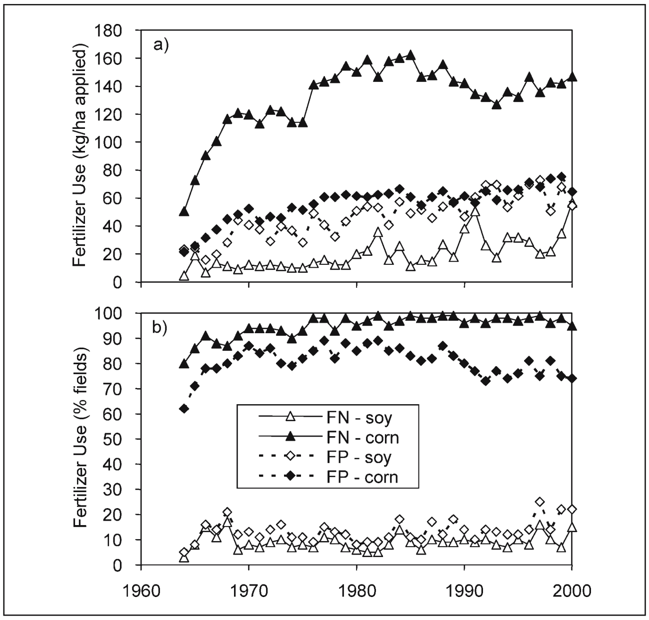

Fig. 2: Historical nutrient use of commercial nitrogen (FN) and phosphate (FP) fertilizers for corn and soy in Iowa: a) application rate; and, b) fraction of fields applying fertilizer

(0.35±0.06) of the Cedar River values. This fraction was used to estimate the total nitrogen load to the Mississippi River during the period 1978–1995. TP values for the Wapsipinicon (1978–1995) were estimated as a fraction (0.062±0.015) of the total loads from other rivers.

Becher et al. [24] provide an estimate of nitrogen sources in Eastern Iowa. They show that a combination of fertilizer nitrogen (FN) and animal manures contribute over 90% of the TN discharged to the Iowa and Skunk Rivers. Thus, we assumed here that the inclusion of animal manures as a TN source would enable us to perform the most accurate calibration. FN used in this region was calculated from published county totals for corn and soy acreage, statewide average FN application rates, and the fraction of farms applying FN to their crops (**Fig. 2**). Animal manure generated within the region was estimated based on county level data for livestock inventory, which were available from the agricultural census on-line for the years of 1988, 1989, 1990, 1992, 1997 and 2002 [28]. Cattle, cows, hogs and sheep were included in the manure calculations. Hogs were observed as having the greatest contribution of manure nitrogen. County averages values were used for the missing years and all years of the validation period (1978–1987). Nutrient composition (N,P) for each type of animal manure was obtained from the USDA Agricultural Waste Field Handbook [29].

2.2 Basis for nutrient leaching model

Previous research efforts to establish empirical formulas to estimate nutrient loads or fluxes to the Mississippi River have incorporated a wide variety of parameters. Some examples include fertilizer application rates in the current and preceding years [16,30,31], total anthropogenic nitrogen inputs [32], residual nitrogen (inputs minus outputs) during the previous year [31], average river discharge rates or stream yield (flow/ watershed area) [31–33], and for phosphorus, the erosion potential [30]. Linear, exponential and other nonlinear equations have resulted from data fitting exercises. In all cases, annual rates or flows were deemed most suitable for these empirical relationships.

Bakhsh et al. [7] found that rainfall was the most significant variable affecting nitrate leaching from a research field in eastern Iowa. They could describe 79% of the total variability in nutrient loads to surface water as a linear function of the annual subsurface drainage volume. Drainage, in turn was linearly related to rainfall.

Review of the TN and TP loads from eastern Iowa to the Mississippi River can help to identify which of these potential variables could be used to provide accurate nutrient load predictions while maintaining a reasonable level of simplicity. Surprisingly, the TN and TP loads from eastern Iowa watersheds to the Mississippi River were highly correlated (1978–1995 data for Skunk, Iowa and Cedar Rivers from NOAA/USGS Hypoxia study, Table 1). A linear regression shows that TN loads for these three rivers are 23.3 times higher than TP loads (R^2=0.88). This indicates that, even with the greater solubility and much more complex transformation processes possible with nitrogen species, it behaves in a similar fashion to phosphate species. The TN and TP loads for these three rivers are also highly correlated to the average annual river flow rate (R^2=0.90, 0.91, respectively). Given the preponderance of evidence that water transport processes dominate the delivery of fertilizer nutrients to surface water bodies, it was hypothesized that a simple linear function that predicts nutrient loading as a function of rainfall – used here as a surrogate for river flowrates – would capture the predominant mechanisms controlling these average annual flows and enable accurate prediction of TN and TP loads to the Mississippi River.

2.3 Mathematical form for the nutrient leaching model

Nutrient flows to the Mississippi River were calculated with a standard emission factor approach with the adaptation that the emission factors varied as a function of rainfall. The general leaching models for TN and TP are defined based on a fraction of the applied nutrient load. The nitrogen model is amended to account for the subsequent loss of nitrate via denitrification in tile drains and local streams.

$$L^N_{MS} = \sum_{j=county}\left(\left\{\left(L^N_{f_j}+L^N_{an_j}\right)\cdot f^N_{SW_j}\right\} - \left\{\left(L^N_{f_j}+L^N_{an_j}\right)\cdot f^N_{SW_j}\right\}\cdot f_{TN,NO3}\cdot f_{de,ri}\right) \quad (1)$$

$$L^P_{MS} = \sum_{j=county}\left(\left(L^P_{f_j}+L^P_{an_j}\right)\cdot f^P_{SW_j}\right) \quad (2)$$

Where L is the mass load (t y^{-1}) for the region with superscripts defining the nutrient (N or P) and subscripts defining the mass discharged to the Mississippi (MS) or added to the system as commercial fertilizer (f) or animal manure (an). The f terms are emission factors that define fractions of the total flows. Subscripts define the fraction of the applied nu-

trient leached to the surface water (SW), the fraction of the total nitrogen that is nitrate (TN,NO3), and the fraction of nitrate in the surface water that is denitrified within the smaller rivers before discharge to the Mississippi River (de,ri). Terms with subscript j are quantified at the county level.

The commercial fertilizer loads for each county (L_f^k) were estimated based on appropriate historical values for the area planted ($A_{i,p}$) (ha) multiplied by the fertilizer application rates ($N_{f,i}$) (t ha^{-1} y^{-1}) and fraction of hectares fertilized ($f_{f,i}$).

$$L^k_{f_j} = A_{c,p_j} \cdot N^k_{f,c} \cdot f^k_{f,c} + A_{soy,p_j} \cdot N^k_{f,soy} \cdot f^k_{f,soy} \tag{3}$$

Subscripts c and soy refer to corn and soybeans, respectively and superscript *k* refers to nitrogen or phosphorus. Data for the area planted in each crop were available for each year at the county level. Fertilizer application rates were available only at the state level and were assumed to be representative for the eastern region. These data, acquired from standard agricultural databases, [34–35] are summarized in Fig. 2.

Eq. (1) and (2) also require estimates of the fraction of nitrogen or phosphorus fertilizer that leaches to the surface water for each county (f_{sw}^k). These terms were estimated as a linear function of rainfall:

$$f^k_{SW_j} = b^k + m^k \cdot R_j \tag{4}$$

Where m and b are the slope and intercept of a linear function, and R_j is the annual rainfall (mm), determined at the centroid of each county [36]. The linear coefficients in Eq. (4) and denitrification rates ($f_{de,ri}$) (Eq. (1)) were calibrated by minimizing the difference in the cumulative mass loading between the nutrient leaching model predictions (Eqs. (1)–(4)) and actual TN and TP loads to the Mississippi over the 11 year period used for to calibrate the model (1988–1998). Two key assumptions were made in this analysis:

1. The same fraction of the nutrients leaches from animal manure and inorganic commercial fertilizer. This assumption is also use in the IPCC nitrogen flow model.
2. Denitrification of NO_3 in rivers also varies some with rainfall [37]. The fraction of the TN that is NO_3 was required to estimate denitrification. This fraction was defined as an average for watershed discharge data available 1988–1998, with a weighted average between the three rivers ($f_{TN,NO3}$ = 0.83).

2.4 Allocation of nutrient leaching flows

In an LCI, it is important to not only quantify flows through the environmental compartments, but also to allocate specific fractions of the total flows among the various products and by-products generated. This is particularly difficult in an agricultural system when there are synergistic affects associated with crop rotation. Van Zeijts et al. [38] address this issue for allocating fertilizer among various crops in the Netherlands. Their overall approach is used here as well. They assume:

- All nitrogen can be allocated to the crop for which it is applied in the year that it is applied
- All P and K fertilizers should be allocated among the crops over the entire crop rotation in proportion to the fraction of nutrient that is harvested with each of the grains.

They justify the differences in these approaches based on the intent of the fertilizer application and its environmental fate. Nitrogen, for example, is typically applied separately for each crop in proportion to that crops needs. Excess fertilization is avoided due to its likely loss to leaching. Phosphate, however, behaves differently. Excess nutrients applied as fertilizer for one crop is conserved in the soil over a longer period. It is often applied only to one crop with the intent that it be consumed by the plants over the entire rotation. The consistency in the percentage of fields onto which nitrogen fertilizer (FN) and phosphate fertilizer (FP) are applied (see Fig. 2) illustrates that indeed, many farmers chose not to apply FP to fields in a soy rotation year, even though the soy beans need phosphorus for growth. These farmers rely on FP remaining in the soil from the previous year.

The suitability of the Van Zeijts et al. [38] approach for nitrogen allocation between corn and soybeans could be argued. Nitrogen fixation by soy increases the nitrogen content in the soil and the soil mineralization rate during soy and corn years, thus providing extra nitrogen that would not otherwise be available [39]. Likewise, excess nitrogen applied to the soil during a corn year and immobilized with in soil organic matter could become available to soy plants in the following year [40]. The 'carry over' of nitrogen fertilizer is indeed observed in leaching rates that are generally no different on a kg/ha basis in years that corn is grown versus years that soy is grown [5,7]. Thus, the approach used by van Zeijts et al. [38] for nitrogen allocation is simplistic.

An alternative approach for allocating the amount of fertilizer nitrogen (FN) leached from corn and soy fields can be based on field data that quantifies actual leaching rates from corn fields versus soy fields. Data from each of the studies at the Nashua IA agricultural testing facility [5,7,41] indicate that even though little to no FN is applied to soy fields, nitrate fluxes (t ha^{-1} y^{-1}) in a given year are approximately equal from each type of field. Statistical analysis showed that there are no trends in the fraction of nitrate that leaches from corn fields as a function of year or tillage practices (α=0.05). Thus, all data were lumped together (n=42) to show that 51.1% (standard deviation = ±7.2) of the total amount of nitrate that leached on a per hectare basis could be allocated to the corn. The total mass of nitrogen discharged to the Mississippi River from commercial fertilizers used in eastern Iowa that can be allocated to corn ($L^N_{MS,c}$; t y^{-1}) can be determined as an area weighted average, with slightly higher losses from corn fields:

$$L^N_{MS,c} = \frac{\sum\limits_{j=county} A_{c,p_j}}{\sum\limits_{j=county}\left\{A_{c,p_j} + \left(\frac{1-f_{N-leach,c}}{f_{N-leach,c}}\right)\cdot A_{soy,p_j}\right\}} \cdot \sum_{j=\mathrm{county}}\left(L^N_{f_j}\cdot f^N_{SW_j}\cdot\left(1-f_{TN,NO3}\cdot f_{de,ri}\right)\right) \tag{5}$$

where the fraction allocated to corn ($f_{N\text{-}leach,c}$) was set at 51%. The summation on the right represents the commercial fertilizer component of Eq. (1).

3 Results and Discussion

3.1 Nutrient leaching model

The nutrient leaching models for TN and TP (Eqs. (1)–(4)) were calibrated independently. The calibrated model estimates are within 1.1% of the actual cumulative TN load and 0.3% for the total mass of TP discharged over the 11 years. Values for the calibrated model parameters used are included in **Table 2**. The model estimates for L^N_{MS} and L^P_{MS} were very sensitive to the slope, intercept and rain data used in the regression equations. Very small modifications in the slope and intercept helped substantially to improve the quality of the fit. Application of the high denitrification rates ($f_{de,ri}$) suggested by deVries et al. [16] for the Netherlands resulted in very low estimates of nutrients discharged to the Mississippi (L_{MS}). Thus, lower denitrification rates were required in both high and low flow years to calibrate the model. The TN model was not very sensitive to the fraction of the total nitrogen that is in the form of nitrate ($f_{TN,NO3}$), so this parameter was not adjusted.

Table 2: Calibrated emission factors used in the nutrient leaching models

Model Parameter	Calibrated Value	Comments
Nitrogen leaching model (Eq. (1), (4))		
Intercept	–0.545	Highly sensitive to small changes
Slope	0.000975	Highly sensitive to small changes
$f_{TN,NO3}$	0.83	Not sensitive
$f_{de,ri}$	0.2	For years with high flow – highly sensitive
$f_{de,ri}$	0.3	For years with low flow. (<900 mm)
Phosphorus leaching model (Eq. (2) and (4))		
Intercept	–0.11	Highly sensitive to small changes
Slope	0.000174	Highly sensitive to small changes

Fig. 3 presents the model predictions and actual TN and TP loads to the Mississippi River. The low TN and TP loadings in 1988 and 1989 correspond to drought years and the very high loadings in 1993 correlated to heavy rains and flooding. With a few exceptions, the calibrated model represents both the trends and the absolute value of the TN and TP loads. For individual years, the greatest percent errors in TN loads were for 1988 (–88%) and 1989 (+160%). 1988 resulted in the greatest error for TP loads as well (–99%), although it is apparent that the absolute errors in these years were small. Calibrated estimates of TN loads for seven of the years were within 25% of the loads determined from water quality data.

The calibrated model was applied to the 1978–1987 period for validation (see Fig. 3; open circles). Both the TN and TP predicted loads were very representative of the trends and value of the actual loads to the Mississippi River. For TP loads, the absolute value of errors in the annual loads ranged from 0.15% (1983) to 104% (1985), with the error for the cumulative 11 year load 20%. Similar results were obtained for the TN model. The maximum error in the annual load was 95% (1981). Both the fact that predictions for seven of the ten years were within 25% of the actual data and the ten-year cumulative load within 14% of the actual load verify the validity of this relatively simple approach for estimating nutrient loading to surface water from fertilizer use on row crops.

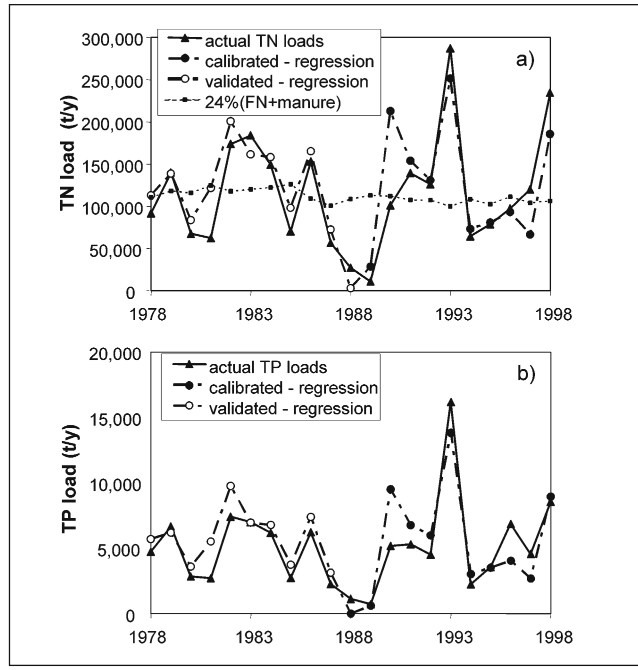

Fig. 3: Actual and predicted loads of total nitrogen (a) and total phosphorus (b) from eastern Iowa watersheds to the Mississippi River. Solid circles represent the calibrated model and open circles show the model validated against data not used for the calibration process

The quality of the nitrogen leaching model presented here can also be assessed by comparing the emission factor for leaching (f^N_{SW}) and the nitrogen yields to those measured by others. Over the entire region, the model presented here estimates the load of TN to surface waters through tile and base flow to be 6.4–85% of the applied fertilizer. Distributions of these emission factors at the county level for both nitrogen and phosphorus are presented in **Fig. 4**, along with

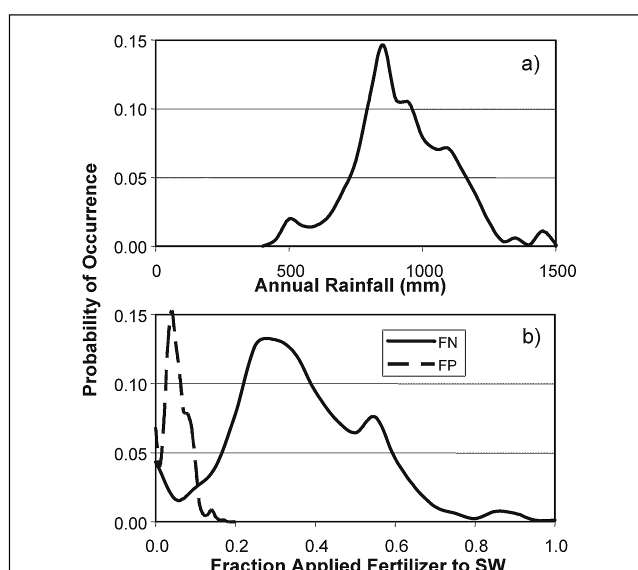

Fig. 4: Histograms illustrate the distribution of county-level rainfall (a) and the fraction of nitrogen and phosphate fertilizers that are delivered to surface water bodies

Table 3: Range of estimates – emission factors for quantifying fraction of commercial nitrogen fertilizer that leaches with water

Emission Factor	Comments, references
0.316	**Median – this study (Fig. 4)**
0.24	Used in LCA for subsequent denitrification and N_2O emissions for transportation fuels (GREET [15])
0.30	Global average value used for subsequent denitrification and N_2O emission (IPCC [19])
0.25 (0.015–0.64)	Measured at downstream location. Estimated from cumulative load in Raccoon River (central IA) over 11 years versus cumulative FN used. [3]
0.36 (0.08–0.59)	Measured – 3 year field scale study. Nashua IA [4]
0.26 (0.05–0.76)	Measured – 6 year field scale study. Nashua IA (NE IA). Rainfall rates most significant variable [5]
0.42 (0.09–0.85)	Measured – Walnut Creek watershed study, central IA, average of several drainage-scale systems [6]
0.47	Overall 6 year cumulative average fraction FN leached from single C-S rotation field in Walnut Creek watershed, central IA (1992–1997) [6]

the correlated distribution of rainfall. As expected based on the lower solubility of phosphates, a much smaller fraction of phosphate fertilizer enters the surface water than of nitrogen fertilizer. The median of emission factors for nitrogen (0.32; **Table 3**) is within the range of averages presented by others (0.24–0.47). The skewed distribution for nitrogen leaching shown in Fig. 4 exemplifies the importance of predicting much higher nutrient loads during rainy years.

When the amount of nitrogen leached is presented as a yield (kg ha^{-1} y^{-1}), predicted TN loads are also quite comparable to other studies from the Midwestern United States (**Table 4**). Given the consistency of the yields predicted with the nitrogen model used here and those measured by others, and the accuracy of the validated TN leaching model (see Fig. 3), the estimated discharges of TN from row crops and to the Mississippi River are considered realistic.

The model estimates of the fraction of the fertilizer phosphorus that leaches, ~0–12% (median 4.2%, see Fig. 4), compares quite well with global estimates of phosphorus fertilizer leaching rates (1–5%) [42] and those measured in a limited number of field studies in Iowa (5–15%) [43].

Table 4: Comparison of nitrogen yields estimated with the leaching model and those measured by others

Range of Values (kg-N/ha crop/yr)	Comments, references
5.8–64	**TN – This study (median: 32 kg/ha)**
38–64	NO_3-N in tile drain water, IL 30-ha field [51]
11–107	NO_3-N in tile waters, 4 different tillage systems in IA [41]
4–46	NO_3-N in tile waters, field study in IA [7]
2–60	NO_3-N in tile waters, 8 year watershed study, IA [33]
10–80	TN from OH watershed [52]
38±16	Model results for corn in Midwest USA [17]
22±13	Model results for soybeans in Midwest USA [17]

The approach used by LCI models such as GREET [15] (TN leaching = $0.24 \cdot L_f$) provides an excellent estimate of the TN load for 'average' years (see Fig. 3). However, the use of a constant emission factor does not capture the wide variability in leaching rates that are correlated to rainfall. Errors with the GREET approach are as high as 900% (1989), with an overall average and standard deviation of errors over the 21 year period of –66%±211%. In contrast, the average error with the variable leaching model developed here is –17%±53%. The biggest concern with the use of a constant emission factor for nitrogen leaching is the inability of this approach to predict the extremely high nutrient loadings that occur in rainy years. The actual loads in 1993 were over three times the value predicted using the GREET emission factor. The extreme nutrient loads that occurred in 1993 led to a record size of the hypoxic zone in the Gulf of Mexico (18,000 km^2) [2]. The ability to accurately predict extreme LCI nutrient loads with the model proposed here will also lead to an improved ability to predict their related environmental impacts.

3.3 Allocating nutrient flows between corn and soybeans

The allocation process is an important step to define of how much of the total environmental emissions can be attributed to corn versus soybean. Estimates of the TN leached that can be allocated to corn between the two methods considered here ranged from 60±4% (Eq. (5)) to 98±1% (Van Zeijts et al. [38] method). The balance of the TN load is allocated to soybeans. The difference between these methods stems from a poorly understood symbiosis of nitrogen flows within the corn-soybean rotation that is difficult to integrate into an LCA. The allocation of phosphorus between crops shows that 61±4% should be allocated to corn in this system. The standard deviations in the above numbers represent variability between different years. Unlike the total load of nutrients discharged, there is little variability in the fraction of nutrients allocated between the crops among years with variable rainfall.

3.4 Eutrophication impact

In life cycle assessments, equivalency factors are often used to aggregate nitrogen and phosphorus species to quantify the overall eutrophication potential. The Redfield molar ratio (16:1) for the N:P content in aquatic cell mass is used here to quantify the equivalency factors [44]. In reality, water bodies have a broad range of ratios in the limiting N:P ratios that enable excess algal growth and eutrophication [45]. For example, a higher N:P ratio of 22:1 can apply to eutrophic waters [46].

The eutrophication potential (t y^{-1}as NO_3-N equivalents) discharged to local streams and then the Mississippi River includes total nitrogen and total phosphorus loads predicted from the calibrated leaching models. This potential is compared to several different benchmarks to define the potential impact of these discharges. Bench marks include:

- Median background concentration of TN (0.13 mg/L) and TP (0.021 mg/L) in streams and rivers in the corn belt region and great plains [47]
- Proposed water quality standards for TN (2.18 mg/L) and TP (0.0763 mg/L) in the corn belt region [48,49]
- Recommended 30% reduced load of 1980–1996 average TN load to the Gulf of Mexico to reduce hypoxia [50]

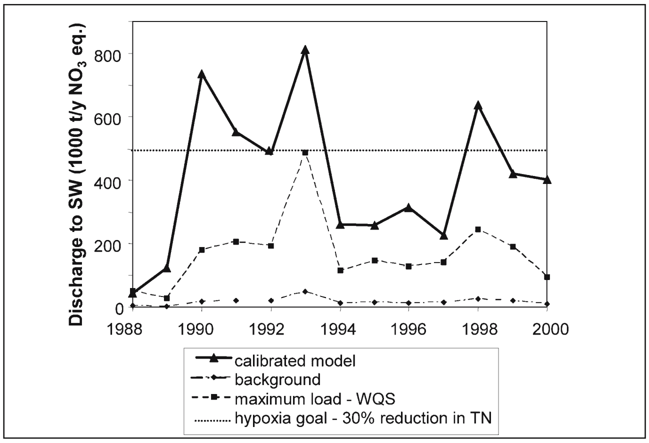

Fig. 5: Predicted eutrophication impact based on calibrated leaching models compared with various benchmarks

Concentration limits were multiplied by the actual annual mean stream flow rate and converted to an eutrophication potential (TN+TP, as NO_3-N) to determine the load.

The estimated eutrophication potential for the period 1988–2000 is compared to the applicable benchmarks in **Fig. 5**. The total modeled eutrophication potential is much higher in all years than the load estimated from proposed water quality standards. This indicates that unacceptably high levels of biomass growth, decay, and oxygen depletion will occur in the streams and rivers in eastern Iowa. Utilizing the higher N:P ratio of 22:1 for eutrophic waters would show greater contributions from TP and even higher total eutrophication potentials.

As the nutrients are transported downstream in the Mississippi River, they have additional eutrophication consequences in the Gulf of Mexico where they contribute to hypoxia. The goal of a 30% reduction in the average TN load established by a federally endorsed task force on hypoxia [50] is shown as a straight line at ~500,000 t y^{-1} as NO_3-N. Modeling work by Scavia et al. [14] suggest that the goal set by Brezonik et al. [50] is too low and that a 40–45% reduction in average TN loads would be required to limit the size of the hypoxic zone. The 45% reduction in average TN loads would lower the acceptable eutrophication potential to 421,000 t y^{-1} as NO_3-N.

The eastern Iowa contributions to the total eutrophication potential exceed the 30% reduction goal in 5 of the 13 years shown in Fig. 5. In contrast, the use of a constant emission factor for fertilizer leaching (24%) to estimate the nitrate load to surface water would predict that the eutrophication potential discharged to the Mississippi River is always less than the suggested ~500,000 t y^{-1} NO_3-N target. This example clearly shows the necessity of incorporating the climatic variability in loads on actual environmental impact.

4 Conclusions, Recommendations and Perspective

The nutrient flow model was calibrated and verified for a set of watersheds covering most of the eastern half of Iowa for a 21-year period that includes both drought and flood years. Water quality data were available for these watersheds allowing the TN and TP loads to be calibrated to actual measured discharges. The incorporation of annual variability in nutrient loads due to rainfall has not been used before with LCAs for non-point source pollutants and provides an excellent approach for quantifying the true variability. Although this approach helps to improve the estimates and variability in non-point emissions from nutrient leaching, it also makes the model and approach very site specific. Thus, the specific linear model presented here to estimate the fraction of fertilizer that leaches should not be applied directly to other locations. For example, western Iowa has sandier soil, which would allow a greater mass of nutrients to infiltrate to groundwater, with less to surface water. Although it is not intended that the site specific values presented here be used elsewhere, the general approach and framework is valuable and can be applied to other sites that have suitable water quality data.

The results of this analysis show that the eutrophication potential for the current system already exceeds acceptable limits. TN and TP discharges from row crops in eastern IA exceed the maximum loads defined by the proposed water quality standards every year. Limits established by the goal of a 30% reduction in the average TN load to reduce hypoxia are also exceeded in approximately half of the years.

Lifecycle inventories quantifying non-point source nutrient discharges from corn-soybean production should include the variability in these flows that occur due to climatic conditions. Failure to do so will reduce the LCA's capability of quantifying the very significant eutrophication and hypoxia impacts associated with wet years.

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References

[1] Goolsby DA, Battaglin WA, Lawrence GB, Artz RS, Aulenbach BT, Hooper RP, Keenley DR, Stensland GJ (1999): Flux and sources of nutrients in the Mississippi-Atchafalaya River Basin. Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA, Washington DC, <http://oceanservice.noaa.gov/products/pubs_hypox.html>

[2] Goolsby DA, Battaglin WA (2000): Nitrogen in the Mississippi Basin-Estimating Sources and Predicting Flux to the Gulf of Mexico. USGS Fact Sheet 135-00, <http://ks.water.usgs.gov/Kansas/pubs/fact-sheets/fs.135-00.pdf>

[3] Lucey KJ, Goolsby DA (1993): Effects of climatic variation over 11 Years on nitrate-nitrogen concentrations in the Racoon River, Iowa. J Environ Qual 22, 38–46

[4] Puckett LJ, Cowdery TK, Lorenz DL, Stoner JD (1999): Estimation of nitrate contamination of an agro-ecosystem outwash aquifer using a nitrogen mass balance approach. J Environ Qual, 28, 2015–2025

[5] Weed DAJ, Kanwar RS (1996): Water quality – Nitrate and water present in and flowing from root-zone soil. J Environ Qual 25, 709–719

[6] Jaynes DB, Hatfield JL, Meek DW (1999): Water quality in Walnut Creek watershed: Herbicides and nitrate in surface waters. J Environ Qual 28, 45–59

[7] Bakhsh A, Kanwar RS, Bailey TB et al. (2002): Cropping system effects on NO3-N loss with subsurface drainage water. T ASAE 45, 1789–1797
[8] Turner RE, Rablais NN (1994): Coastal eutrophication near the Mississippi River Delta. Nature 368 619–621
[9] Arnold JG, Srinivasan R, Muttiah RS, Williams JR (1998): Large area hydrologic modeling and assessment – Part 1: Model development. J Am Water Resourc As 34, 73–89
[10] Williams JR, Jones CA, Kinery JR, Spanel DA (1989): The EPIC crop growth model. T ASAE 32, 497–511
[11] Vache KB, Eilers JM, Santelmann MV (2002): Water quality modeling of alternative agricultural scenarios in the US corn belt. J Am Water Resourc As 38, 773–787
[12] Kirchner JW, Feng X, Neal C (2000): Fractal stream chemistry and its implications for contaminant transport in catchments. Nature 403, 524–527
[13] Rinaldo A, Botter G, Bertuzzo, E, Uccelli A, Settin T, Marani M (2005) Transport at basin scales: 2. Applications. Hydrol Earth Sys Sci Discuss 2, 1641–1681
[14] Scavia D, Rabalais NN, Turner RE, Justic D, Wiseman WJ, Jr (2003): Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. Limnology Oceanography 48, 951–956
[15] Wang MQ (1999): GREET 1.5 – Transportation Fuel-Cycle Model, Volume 2: Appendices of data and results. Argonne National Laboratory, Argonne, IL, ANL/ESD-39
[16] deVries W, Kros J, Oenema O, deKlein J (2003): Uncertainties in the fate of nitrogen. Nutrient Cycling in Agrosystems 66, 71–102
[17] Miller SA, Landis AE, Theis TL (2006): Use of Monte Carlo analysis to characterize nitrogen fluxes in agroecosystems. Environ Sci Technol 40, 2324–2332
[18] Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T, Berendse F, Freney J, Kudeyarov V, Murdoch P, Zhu ZL (1996): Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35, 75–139
[19] IPCC (1996): IPCC Guidelines for National Greenhouse Gas Inventories, Reference Manual (Vol. 3) <http://www.ipcc-nggip.iges.or.jp/public/gl/invs6.html>
[20] Gast RG, Nelson WW, Randall GW (1978): Nitrate accumulation in soils and loss in tile drainage following nitrogen applications to continuous corn. J Environ Qual 7, 258–261
[21] Hallberg GR (1987): Nitrates in Iowa Groundwater. In: D'Itri FM, Wolfson LG (eds), Rural Groundwater Contamination. Lewis Publishers Inc., Chelsea MI, Chapter 3, pp 23–68
[22] Sheehan J, Camobreco V, Duffield J, Graboski M, Shapouri H (1998): Life Cycle Inventory of Biodiesel for use in an Urban Bus. Final Report prepared by the National Renewable Energy Laboratory (NREL/SR-580-24089)
[23] Sheehan J, Aden A, Paustian K, Killian K, Brenner J, Walsh M, Nelson R (2003): Energy and Environmental Aspects of Using Corn Stover for Fuel Ethanol. J Industrial Ecol 7, 117–146
[24] Becher KD, Schnoebelen DJ, Akers KKB (2000): Nutrients discharged to the Mississippi River from Eastern Iowa Watersheds, 1996-1997. J Am Water Resour As 36, 161–173
[25] Becher KD, Kalkhoff SJ, Schnoebelen, DJ, Barnes KK, Miller VE (2001): Water-quality assessment of the Eastern Iowa Basins – Nitrogen, phosphorus, suspended sediment, and organic carbon in surface water, 1996–98. U.S. Geological Survey Water-Resources Investigations Report 01-4175
[26] Brenner J, Paustien K, Bluhm G, Cipra J, Easter M, Elliott T, Kautza T, Killian K, Schuler J, Williams S (2001): Quantifying the change in greenhouse gas emissions due to the natural resource conservation practice application in Iowa. Final report prepared for the Iowa Conservation Partnership. Colorado State University Natural Resource Ecology Laboratory, Fort Collins CO
[27] USGS Hypoxia in the Gulf of Mexico: website <http://co.water.usgs.gov/hypoxia/html/nutrients.html>, accessed December 2005
[28] USDA Agricultural Census data. <http://usda.mannlib.cornell.edu:8080/MannUsda/viewDocumentDirectory.do?documentID=109> , accessed June 2005
[29] USDA Natural Resources Conservation Service. Agricultural Waste Management Field Handbook. Chapter 4: Animal Waste Characteristics, <ftp://ftp.wcc.nrcs.usda.gov/downloads/wastemgmt/AWMFH/awmfh-chap4.pdf>
[30] Sharpley AN, McDowell RW, Weld JL, Kleinman PJA (2001): Assessing site vulnerability to phosphorus loss in an agricultural watershed. J Environ Qual 30, 2026–2036
[31] Goolsby DA, Battaglin WA (2001): Long-term changes in concentration and flux of nitrogen in the Mississippi River Basin, USA. Hydrol Process 15, 1209–1226
[32] McIsaac GF, David MB, Gertner GZ, Goolsby DA (2002): Relating net nitrogen input in the Mississippi River basin to nitrate flux in the lower Mississippi River: A comparison of approaches. J Environ Qual, 31 1610–1622
[33] Tomer MD, Meek DW, Jaynes DB, Hatfield JL (2003): Evaluation of nitrate nitrogen fluxes from a tile-drained watershed in central Iowa. J Environ Qual 32, 642–653
[34] USDA National Agricultural Statistical Services: data base, <http://www.usda.gov/nass/pubs/histdata.htm>, accessed March 2004
[35] USDA Census reports: <http://agcensus.mannlib.cornell.edu/>, accessed March 2004
[36] Spatial Climate Analysis Service: <http://www.ocs.orst.edu/prism/>, accessed March 2004
[37] Smith RA, Schwarz GE, Alexander RB (1997): Regional interpretation of water-quality monitoring data. Water Resour Res 33, 2781–2798
[38] Van Zeijts H, Leneman H, Wegener-Sleeswijk A (1999): Fitting fertilization in LCA: Allocation to crops and cropping plan. J Cleaner Prod 7, 69–74
[39] Gentry LE, Below FE, David MB et al. (2001): Source of the soybean N credit in maize production. Plant Soil 236, 175–184
[40] Baker JL, Timmons DR (1994): Effect of fertilizer management on leaching of labeled nitrogen for no-till corn in field lysimeters. J Environ Qual 23, 305–310
[41] Bjorneberg DL, Kanwar RS, Melvin SW, (1996): Seasonal changes in flow and nitrate-N loss from subsurface drains. T ASAE 39, 961–967
[42] Smil V (2000): Phosphorus in the environment: Natural flows and Human interferences. Annu Rev Energy Environ 25, 53–88
[43] Klatta JG, Mallarino AP, Downing JA, Kopaskab JA, Wittrya DJ (2003): Soil phosphorus, management practices, and their relationship to phosphorus delivery in the Iowa Clear Lake agricultural watershed. J Environ Qual 32, 2140–2149
[44] Hauschild MZ, Wenzel H (1998): Environmental Assessment of Products. Volume 2: Scientific Background. Chapman and Hall, London
[45] Seppala J, Knuuttila S, Silvo K (2004): Eutrophication of Aquatic Ecosystems: A new method fpr calculating the potential contributions of nitrogen and phosphorus. Int J LCA 9, 90–100
[46] Klaff J (2003): Limnology. 2nd ed., Prentice-Hall, Englewood Cliffs, NJ
[47] Smith RA, Alexander RB, Schwarz GE (2003): Estimating the natural background concentrations of nutrients in streams and rivers of the conterminous United States. Environ Sci Technol 37, 3039–3047
[48] USEPA (2000): Nutrient Criteria Technical Guidance Manual – Rivers and Streams. Office of Water, Washington DC (EPA-822-B-00-002), <http://www.epa.gov/ost/criteria/nutrient/guidance/rivers/index.html>
[49] USEPA (2000): Ambient Water Quality Criteria Recommendations – Rivers and Steams in Nutrient Ecoregion VI. Office of Water, Washington DC (EPA-822-B-00-017), <http://www.epa.gov/waterscience/criteria/nutrient/ecoregions/rivers/rivers_6.pdf>
[50] Brezonik PL, Bierman VJ, Alexander R, Anderson J, Barko J, Dortch M, Hatch L, Hitchcock GL, Keeney D, Mulla D, Smith V, Walker C, Whiteledge T, Wiseman WJ (1999): Effects of reducing nutrient loads to surface waters within the Mississippi River basin and Gulf of Mexico. Topic 4 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA, Washington DC, <http://oceanservice.noaa.gov/products/pubs_hypox.html>
[51] David MB, Gentry LE, Kovacic DA et al. (1987): Nitrogen balance in and export from an agricultural watershed. J Environ Qual 26, 1038–1048
[52] Vanni MJ, Renwick WH, Headworth JL, Auch JD, Schaus MH (2001): Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. Biogeochemistry 54, 85–114

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